Low Temperature Magnetoresistance and the Magnetic Phase Diagram of La$_{1-x}$Ca$_x$MnO$_3$

P. Schiffer,* A. P. Ramirez, W. Bao, and S-W. Cheong

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 27 December 1994)

The complete phase diagram of a “colossal” magnetoresistance material (La$_{1-x}$Ca$_x$MnO$_3$) was obtained for the first time through magnetization and resistivity measurements over a broad range of temperatures and concentrations. Near $x = 0.50$, the ground state changes from a ferromagnetic (FM) conductor to an antiferromagnetic (AFM) insulator, leading to a strongly first order AFM transition with supercooling of $\sim 30\%$ $T_N$ at $x = 0.50$. An unexpectedly large magnetoresistance is seen at low temperatures in the FM phase, and is largely attributed to unusual domain wall scattering.

PACS numbers: 72.15.Gd, 75.50.Cc, 75.30.Kz

Recently, there has been a surge of interest [1] in the properties of perovskite rare earth manganates. For a broad range of doping, these materials have a paramagnetic-to-ferromagnetic (FM) transition upon cooling, which is accompanied by a sharp drop in the resistivity. This behavior is usually explained with double exchange (DE) theory [2] based on the exchange of electrons between Mn$^{3+}$ and Mn$^{4+}$ ions. The FM transition temperature ($T_c$) is raised in a magnetic field, and thus the system can be tuned between the low and high conductivity phases by applying a magnetic field. This results in a “colossal” magnetoresistance (CMR) near $T_c$ (as much as 100 000% in thin films) [1], which has a completely different physical origin from the “giant” magnetoresistance observed in layered and clustered compounds.

Despite the long history of work on these materials, there has been no systematic investigation of the properties across the full range of doping or at low temperatures. In this Letter we present the first measurements of the magnetization ($M$) and resistivity ($\rho$) of a CMR material (La$_{1-x}$Ca$_x$MnO$_3$) for $0 < x < 1$ and over a broad range of temperatures and fields. In particular, we obtain the full magnetic phase diagram, and we study the low temperature properties which have not been previously examined in detail. In the doping range of the CMR ($0.15 < x < 0.50$), we observe a significant MR ($\sim 35\%$) at temperatures well below $T_c$, a regime which is ignored in previous theoretical work. At $x = 0.50$, the ground state changes from FM and conducting to antiferromagnetic (AFM) and insulating, leading to a first order AFM transition at $x \sim 0.50$ with large supercooling and strongly hysteretic behavior in $\rho$.

Our samples ($x = 0, 0.10, 0.20, 0.25, 0.33, 0.45, 0.48, 0.50, 0.52, 0.55, 0.60, 0.67, 0.75$, and $1.00$) were synthesized by mixing stoichiometric proportions of La$_2$O$_3$, CaCO$_3$, and MnO$_2$ and then heating in air at $1250^\circ$C for $5\, h$, at $1380^\circ$C for $12\, h$, and at $1390^\circ$C for $20\, h$ with intermediate grindings, and powder diffraction x-ray studies showed clean single-phase patterns. In order to observe the effect of oxygen stoichiometry, some of the samples underwent various heat treatments such as annealing under 200 bars of oxygen pressure at $\sim 600^\circ$C and quenching from $1300^\circ$C, but little change in the physical properties resulted ($\Delta T_c \sim 2\%, \Delta \rho \sim 5\%$). Careful studies of ceramic samples of the doped lanthanum manganates have found the oxygen stoichiometry to be within $< 1\%$ of ideal, following a wide variety of synthesis conditions (including those virtually identical to ours) and cation doping [3]. In fact, preliminary neutron diffraction studies of samples made by our group are consistent with this high degree of stoichiometry [4]. Furthermore, such small (< 1%) differences in oxygen stoichiometry have been found to have little (< 5%) effect on $T_c$ [3]. Magnetization was measured on a commercial SQUID magnetometer, and resistivity was measured by a standard 4 in-line contact technique.

The phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ as a function of $T$ and $x$ is given in Fig. 1. The curved line is drawn as a guide to the eye approximately on the boundary between the spin-disordered paramagnetic state and the spin-ordered states, and the hatched lines indicate the approximate boundaries between different ground states. The various doping regimes are discussed below in order of increasing $x$.

![phase_diagram](image_url)

FIG. 1. The phase diagram of La$_{1-x}$Ca$_x$MnO$_3$, based on the present work. The transition temperatures are taken as the inflection points in $M(T)$ and $\rho(T)$, and $T_N$ for $x = 0.48$ and 0.50 is obtained on warming at $H = 0.1$ T.
For all $x < 0.50$, $M(H)$ at low temperatures increases sharply for $H \lesssim 0.5$ T and then saturates at $\sim 90\%$ of the theoretical single-ion value, behavior typical of domain effects in ferromagnets. For $x = 0$ and $0.10$, the material is FM at low temperatures [5] ($T_c \sim 160$ K) and displays insulating behavior ($d\rho/dT < 0$) at all temperatures measured.

Between $x = 0.20$ and 0.45, the materials displayed CMR behavior, shown in Fig. 2 for $x = 0.25$. The sharp drop of $\rho(T)$ into a low temperature metallic state and the peak in MR are clearly correlated with the FM transition in $M$. For $T > T_c$, observed negative MR and activated resistivity (we find $\rho$ can fit well by $\rho_0 \exp[(2 \times 10^3/T)^{1/4}]$ for $x = 0.25$) have led previous authors to conclude that conduction is by hopping of magnetic polarons [1,6]. In this picture the carriers are coupled to local FM correlations among the Mn ions, and conduction is through hopping between spin-aligned Mn$^{4+}$ sites. We also see an enhancement of the Curie constant [7], which is consistent with the enhanced moments of the polarons. Alternatively, the $T > T_c$ MR was recently explained [8] within an infinite dimensional Kondo model which fit well by $\rho(M)$ in La$_{1-x}$Ca$_x$MnO$_3$. The thermally activated nature of $\rho(T > T_c)$ explains the anomalously large MR (100,000%) observed near $T_c$ by Jin et al. [1] in thin films where $T_c$ was suppressed by substrate-induced strain [9]. This suppression of $T_c$ led to a much higher $\rho$ immediately above the transition, and thus to a much larger drop in $\rho$ at $T_c$ and, consequently, larger MR.

In the CMR doping regime, the behavior of $\rho$ at $T_c$ has been explained by DE models in which Mn$^{3+}$ and Mn$^{4+}$ ions are coupled by electron exchange through the oxygen sites. Models incorporating DE lead to both ferromagnetism and metallic conductivity for sufficient Mn$^{4+}$ density, and nonaligned spins in such models cause strong electron scattering. For temperatures just below $T_c$, DE explains the qualitative features of the data, since $\rho$ drops rapidly while $M$ rises rapidly to near saturation (although detailed agreement is lacking) [10]. At low temperatures ($T \ll T_c$) there have been few explicit theoretical predictions, but most work [2,8,10] implies that MR $\rightarrow 0$ as the spins become aligned in the limit of $T \rightarrow 0$.

In Fig. 2 we have also plotted the negative MR between $H = 0$ T and $H = 0$,

\[
MR(4,0) = \frac{\rho(H = 0 \ T) - \rho(H = 4 \ T)}{\rho(H = 0 \ T)},
\]

as a function of temperature for La$_{0.75}$Ca$_{0.25}$MnO$_3$ (these data show qualitatively the same features as those for $x = 0.20, 0.33$, and 0.45). We see that MR(4,0) $\sim 0.35$ and increasing as $T \rightarrow 0$. Additionally, MR(4,1) $\sim 0.1$ as $T \rightarrow 0$ even though $M(H)$ is saturated above $H = 1$ T due to domain alignment. While low temperature MR at low fields can be understood in terms of domain wall scattering (as discussed below), this low temperature MR at high fields cannot be explained within existing DE theory.

To understand the MR at low temperatures, it is useful to examine $\rho(T)$ in more detail. For $T < 0.5T_c$, [where $M(T)$ indicates that local FM order is $>95\%$ complete], $\rho(T)$ is fit well by the form

\[
\rho(T) = \rho_0 + \rho_1 T^{2.5},
\]

as shown by solid lines in the inset to Fig. 2 (this form fit equally well to the data for $x = 0.20, 0.33$, and 0.45). Here $\rho_0$ is the resistivity due to the domain boundaries and other temperature-independent scattering mechanisms, and the $\rho_1 T^{2.5}$ term is an empirical fit to the data which represents a combination of electron-electron, electron-phonon, and electron-magnon scattering, all of which are expected to be significant in this system. The temperature dependence is not fit well by $\rho_1 T^{4.5}$ alone (the dashed line in the inset to Fig. 2), as was suggested by Kubo and Ohata [10] based on a calculation of electron-magnon scattering, although a combination of terms in $T^2$ (from electron-electron scattering) and $T^4$ would fit the data adequately. Electron-phonon scattering is, however, also expected to be an important cause of resistivity in this temperature range since $\Theta_D \sim 500$ K [11].
The field dependences of the MR at $T = 20$ K and of $\rho_0$ and $\rho_1$ (extracted from least-squares fits to the data) are shown in Fig. 3 for La$_{0.75}$Ca$_{0.25}$MnO$_3$. We find that $\rho_1$ is field dependent at high fields (decreasing by $\sim 15\%$ between $H = 1$ and 4 T), which is rather anomalous since $M(H)$ is saturated for $H > 1$ T, and the application of a few tesla should be only a small perturbation on the exchange fields of order 200 T, which are expected in a ferromagnet with $T_c \sim 250$ K. The field dependence of $\rho_1$ (and resulting MR) at high fields therefore implies either an extremely strong magnetoelastic coupling or a surprisingly high sensitivity of the magnon-electron scattering to external fields. 

What is most striking in Fig. 3, however, is that the bulk of the low temperature MR occurs at low fields ($H < 0.5$ T), where $\rho_0(H)$ decreases sharply and where $M(H)$ indicates that domain magnetizations are aligning with the field. These data strongly imply that the low temperature MR can be largely attributed to domain effects.

Low temperatures domain-based negative MR in other ferromagnets can be due to strain effects on the domains as they are aligned in a field, in which case the magnetoresistance is proportional to $M^2$ [12]. The inset to Fig. 3 demonstrates that this is not the case here. Negative MR in clean ferromagnets has also been explained as electrons passing through domain walls, becoming strongly scattered due to Fermi surface effects [13]. Our measured low temperature $\rho$ of $\sim 10^{-2}$ $\Omega$ cm indicates that the electron mean free paths in this system are $\sim 10$ Å, much smaller than any conceivable domain size, and thus this “clean limit” explanation of domain-based MR also does not apply.

The domain wall contribution to the MR in the CMR materials does probably result from the strong correlation between local FM order and metallic behavior in DE. At low fields, the spins in the domain walls are necessarily not ferromagnetically aligned and thus will create resistance. Since the spin-disordered phase is insulating, it is not surprising that even the small local perturbation from ferromagnetism within the domain walls can lead to significant resistivity, but detailed calculations of this effect do not exist. In a strong field, the domains’ magnetizations are nearly parallel, and thus the domain walls are less of a perturbation away from ferromagnetism. The $T \to 0$ upturn in MR (4,0) is due to the increasing relative contribution to $\rho(T)$ of $\rho_0$ as the thermal scattering freezes out. The low temperature MR is larger than that in the resistivity data from crystalline bulk and thin film samples which have somewhat lower resistivity [1,8]. This suggests that the MR may be enhanced by the small grain size within our ceramic samples, leading to more magnetic domains, a result which could have technological implications.

As seen from Fig. 1, at $x \sim 0.50$ the ground state becomes an insulating antiferromagnet [14,15]. As seen in Fig. 4, for $0.50 < x < 0.75$ we find [from $M(T)$ for $275 < T < 360$ K] that $\Theta_W > 0$, which suggests that FM exchanges between the spins are dominant. At lower temperatures there is a transition, presumably to the AFM state, seen in Fig. 4 as a drop in $M$ at what we label the Néel temperature ($T_N$). Also at $T_N$, we see an inflection in $\rho(T)$ which corresponds to a sharp peak in $d[\ln(\rho)]/d(T)$, such as one expects to see at a charge ordering transition [16]. This suggests that a charge-ordering at $T_N$ suppresses ferromagnetism being produced by DE effects at higher temperatures, allowing the system to enter an AFM state. The existence of charge ordering might also explain the maximum in $T_N(x)$ in the phase diagram, since charged superlattices would presumably be favored at a particular population of Mn$^{3+}$ and Mn$^{4+}$ ions.

The behavior at dopings near the transition from a FM to an AFM ground state is particularly curious, as suggested by ambiguous neutron scattering data [15]. At

![FIG. 3. The field dependence of $\rho_0$, $\rho_1$, and MR(H,0) at $T = 20$ K for La$_{0.75}$Ca$_{0.25}$MnO$_3$ (similar results were obtained for $x = 0.20$, 0.33, and 0.45). The inset shows MR(H,0) as a function of $M^2$ at $T = 5$ K, demonstrating nonlinearity.](image-url)

![FIG. 4. The magnetization of La$_{1-x}$Ca$_x$MnO$_3$ at 4 T measured on warming. The inset shows $1/M$ vs $T$, and the straight lines indicate $\Theta_W > 0$ at each doping.](image-url)
$x = 0.45$, $M(T \to 0)$ reaches almost full FM saturation as one would expect for a FM ground state. For $x = 0.48$, there appears to be a FM transition at $\sim 230$ K and then a small drop in $M$ at $\sim 190$ K. At $x = 0.50$, there again appears to be a FM transition, but then $M$ drops sharply to a small fraction of full saturation, presumably indicating the transition to a fully AFM state. For both $x = 0.48$ and 0.50, the existence of an intermediate temperature FM state is indicated by $M(H)$ saturating for $H \geq 2$ T and rise of $M$ to a large fraction ($\sim 70\%$) of the full ferromagnetic moment, behavior which is not observed for $x > 0.50$.

For $x > 0.50$, there is no observed difference between $M(T)$ measured on warming and cooling, suggesting that the transitions to and from the AFM state are second order. For $x = 0.48$ and 0.50, however, the temperatures at which the transitions to and from the AFM state occur ($T_{AFM}$) vary greatly ($\sim 50$ K) between cooling and warming, as demonstrated in Fig. 5, implying a strongly first order transition. What differentiates these two doping levels from the higher values of $x$ is that they undergo a FM transition at high temperatures, rather than merely developing some short-range FM order. The AFM transition is thus from one spin-ordered state to another, the change in symmetry leading to first order behavior. We observed no measurable dependence of $T_{AFM}$ on the rate of cooling/warming, but we find that $T_{AFM}$ is suppressed in a magnetic field ($\Delta T_{AFM} \sim 20$ K between 0.1 and 2.0 T) on both cooling and warming, presumably because the Zeeman energy is lower in the FM state. The first order transition is accompanied by a dramatic difference of almost two orders of magnitude in $\rho$ between cooling and warming near $T_N$ as shown in Fig. 5 for $x = 0.50$. The FM state at $x = 0.50$ does not appear to be conducting, as $\partial \rho/\partial T < 0$ in the FM regime, implying that rather different processes govern the resistivity from those which are active at lower doping levels.

In conclusion, we have obtained the first full phase diagram for a CMR material. In particular, we have begun to elucidate the rather curious behavior near $x = 0.50$, where the ground state changes from FM metallic to AFM insulating. Further details of the magnetic structure near this composition await neutron scattering experiments. We have also observed large low temperature MR, not anticipated by current theoretical models. This MR exists over a broad temperature range and at low magnetic fields, and is thus potentially more technologically relevant than the colossal MR near $T_c$.


Note added.—Since the submission of this paper, related results have been published by Ju et al. (Ref. [3]) and Y. Tomioka et al. [Phys. Rev. Lett. 74, 5108 (1995)].